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Competing Exchange Interactions in the Multiferroic and Ferrimagnetic CaBaCo$_4$O$_7$*


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Competing exchange interactions can produce complex magnetic states together with spin-induced electric polarizations. With competing interactions on alternating triangular and kagome layers, the swedenborgite CaBaCo$_4$O$_7$ may have one of the largest measured spin-induced polarizations of $\sim 1700$ nC/cm$^2$ below its ferrimagnetic transition temperature at 70 K. Upon rotating our sample about $c = [0, 0, 1]$ while the magnetic field is fixed along $[1, 0, 0]$, the three-fold splitting of the spin-wave frequencies indicates that our sample is hexagonally twinned. Magnetization measurements then indicate that roughly 20% of the sample is in a domain with the $a$ axis along $[1, 0, 0]$ and that 80% of the sample is in one of two other domains with the $a$ axis along either $[-1/2, \sqrt{3}/2, 0]$ or $[-1/2, -\sqrt{3}/2, 0]$. Powder neutron-diffraction data, magnetization measurements, and THz absorption spectroscopy reveal that the complex spin order in each domain can be described as a triangular array of bitetrahedral $c$-axis chains ferrimagnetically coupled to each other in the $ab$ plane. The electric-field dependence of bonds coupling these chains produces the large spin-induced polarization of CaBaCo$_4$O$_7$.

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I. INTRODUCTION

Competing exchange interactions produce complex magnetic states with a wide range of interesting behavior found in spin glass 1, spin ice 2, and magnetic skyrmions 3. In multiferroic materials, complex spin states can exhibit a spin-induced electric polarization $P$ due to either the spin current, $p-d$ orbital hybridization, or magnetostriction [4]. Because the coupling between the electrical and magnetic properties in multiferroic materials is both scientifically and technologically important, the effects of competing exchange interactions have been investigated in a wide range of multiferroic materials such as $RMnO_3$ [5], CoCrO$_2$ [6], CuCrO$_2$ [6], CuFeO$_2$ [6], and MnWO$_4$ [8]. While the first four materials [6]–[8] are geometrically frustrated due to competing interactions on a triangular lattice, MnWO$_4$ [10] exhibits long-range competing interactions [11] on a highly-distorted monoclinic lattice.

Compounds in the “114” swedenborgite family [12] R$BaM_4$O$_7$ ($M =$ Co or Fe) contain alternating triangular and kagome layers, both of which are geometrically frustrated when undistorted. The “114” cobaltites [13–15] were initially studied to find charge ordering among the Co$^{2+}$ and Co$^{3+}$ ions. An important member of this family, YBaCo$_4$O$_7$ exhibits antiferromagnetic ordering below 110 K and diffuse scattering [13,14] indicative of spin disorder below 60 K. The magnetic state between 110 K and 60 K is stabilized by a structural transition [18] that relieves the geometric frustration. Both structural and magnetic transitions are quite sensitive to excess oxygen and no magnetic order [18] appears in YBaCo$_4$O$_{7+\delta}$ for $\delta \geq 0.12$. Another family member, YbBaCo$_4$O$_7$ undergoes a structural transition at 175 K that stabilizes an antiferromagnetic state below 80 K [21].

A particularly interesting “114” cobaltite, CaBaCo$_4$O$_7$ undergoes an orthorhombic distortion [22] that relieves the geometric magnetic frustration on both the kagome and triangular layers sketched in Fig. 1 above the magnetic transition temperature $T_c =$ 70 K. Below $T_c$, CaBaCo$_4$O$_7$ develops a very large spin-induced polarization $\sim 1700$ nC/cm$^2$ [24], second only to the conjectured [25] spin-induced polarization $\sim 3000$ nC/cm$^2$ of BiFeO$_3$. Also unusual, CaBaCo$_4$O$_7$ displays a substantial ferrimagnetic moment of about 0.9 $\mu_B$ per formula unit (f.u.) [26], which could allow magnetic control of the

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electric polarization. Although its ferroelectric transition is inaccessible and its permanent electric polarization is not switchable \cite{21}, applications of CaBaCo$_4$O$_7$ might utilize the large spin-induced polarization produced by a magnetic field just below $T_c$ \cite{22}.

This paper examines the magnetic properties of CaBaCo$_4$O$_7$ based on a Heisenberg model with 12 nearest neighbor interactions and associated anisotropies. The magnetic state of CaBaCo$_4$O$_7$ can be described as a triangular array of ferrimagnetically aligned, bitetrahedral $c$-axis chains with net moment along $b$. Competing interactions within each chain produce a non-collinear spin state. The strong electric polarization of CaBaCo$_4$O$_7$ below $T_c$ is induced by the displacement of oxygen atoms surrounding bonds that couple those chains.

This paper has six sections. Section II proposes a microscopic model for CaBaCo$_4$O$_7$. New magnetization and optical measurements are presented in Section III. Fitting results are discussed in Section IV. In Section V, we predict the spin-induced electric polarization. Section VI contains a conclusion.

\section{Microscopic Model}

Each magnetic unit cell of CaBaCo$_4$O$_7$ contains 16 Co ions on two kagome and two triangular layers with orthorhombic lattice constants $a = 6.3$ Å, $b = 11.0$ Å, and $c = 10.2$ Å. Four crystallographically distinct Co ions have three different valences \cite{22,23}. Triangular layers contain mixed-valent Co$^{3+}$/Co$^{2+}$ \cite{24} (\(L\) is a ligand hole) spins 1, 5, 9, and 13 with moments $M_1 = 2.9 \mu_B$. Kagome layers contain Co$^{2+}$ spins 2, 3, 6, 7, 10, 11, 14, and 15 with moments $M_2 = M_3 = 2 \mu_B$ and mixed-valent Co$^{3+}$/Co$^{2+}$ \cite{24} spins 4, 8, 12, and 16 with $M_3 = 2.4 \mu_B$. Because adjacent kagome or triangular layers are related by symmetry, $S_i = S_{i+4}$ on layer two is identical to $S_i$ on layer one. With $S_i = S_i (\cos \phi_i, \sin \phi_i, 0)$ constrained to the $ab$ plane, the ferrimagnetic moment lies along $b$ if $\phi_i = \pi - \phi_i$ ($i = 1, \ldots, 4$).

The 12 different nearest-neighbor exchange couplings $J_i$ are drawn in Figs. 1(a-b) and 2. Six of these ($J_1$ through $J_6$) couple the kagome and triangular layers as shown in Fig. 2; the other six ($J_7$ through $J_{12}$) couple the spins within a kagome layer as shown in Figs. 1(a) and (b). The dominance of nearest-neighbor exchange over next-nearest neighbor exchange \cite{25} justifies setting the exchange interactions between spins on the triangular layers to zero. Our model also includes easy-plane anisotropies $D$, easy-axis anisotropies $C$ within both kagome and triangular layers, and hexagonal anisotropy $A$ on the triangular layers.

With magnetic field $B$ along $m$, the Hamiltonian is

\begin{align}
\mathcal{H} &= - \sum_{i,j} J_{ij} S_i \cdot S_j + D^{\text{tri}} \sum_{i,\text{tri}} S_i c^2 + D^{\text{kag}} \sum_{i,\text{kag}} S_i c^2 \\
&- C^{\text{kag}} \sum_{i,\text{kag}} (\mathbf{o}_i \cdot S_i)^2 - C^{\text{tri}} \sum_{i,\text{tri}} (\mathbf{n}_i \cdot S_i)^2 \\
&- A^{\text{tri}} \text{Re} \sum_{i,\text{tri}} (S_i a + i S_i b)^6 - g_\mu B \sum_i \mathbf{m} \cdot S_i, \quad (1)
\end{align}

where $S_i$ is a spin $S$ operator on site $i$. For simplicity, we set $g = 2$ for all spins.

The easy-axis anisotropy terms proportional to $C^{\text{kag}}$ and $C^{\text{tri}}$ involve unit vectors $\mathbf{o}_i$ along the “bowtie” directions $\phi_i = \pi/2$ (spins 2 and 6), $5\pi/6$ (spins 3 and 8)
and 7π/6 (spins 4 and 7) for the kagome layers and \( \mathbf{n}_i \)
along the \( \phi_i = \pi/6 \) (spin 1) and \( -\pi/6 \) (spin 5)
directions for the triangular layers. The hexagonal anisotropy on
the triangular layers has expectation value
\[
- A^{\text{tri}} S_1^6 \sum_{i,\text{tri}} \sin^6 \theta_i \cos 6 \phi_i.
\]
All anisotropy terms may act to constrain the spins to
the \( ab \) plane.

Spin amplitudes \( S_n \) are fixed at their observed values \( M_n/2\mu_B \)
per field after performing a 1/\( S \) expansion about the classical limit. Alternatively, the spins \( S_n \) could all have
been taken as 3/2 but with different \( g \)-factors for different sets of spins. As discussed below, that would reduce the estimated exchange coupling \( J_{ij} \) by a factor of \( 4 S_n S_j /9 \).

Static properties are obtained by minimizing the classical energy \( \mathcal{H} \) (the zeroth-order term in this expansion) with respect to the 16 spin angles. The eigenvalues and
eigenvectors of a 32 × 32 equations-of-motion matrix \( [29] \)
produced by the second-order term in the 1/\( S \) expansion
give the optical mode frequencies and absorptions, respectively.

III. MAGNETIZATION AND OPTICAL MEASUREMENTS

Perhaps due to excess or deficient oxygen \( [30] \) or differ-
ent domain populations (see below), previous magneti-
zeation measurements \( [22,26,31–33] \) on CaBaCo\(_4\)O\(_7\) are
rather scattered. Consequently, new magnetization measurements were performed at 4 K on hexagonally-twinned
crystals with a common \( c = [0, 0, 1] \) axis. In domain I, a lies along the laboratory direction \( x = [1, 0, 0] \) and \( b \)
lies along \( y = [0, 1, 0] \); in domain II, \( a = [-1/2, \sqrt{3}/2, 0] \)
and \( b = [-\sqrt{3}/2, -1/2, 0] \); and in domain III, \( a = [-1/2, -\sqrt{3}/2, 0] \) and \( b = [\sqrt{3}/2, -1/2, 0] \). If \( p_1 \) are
the domain populations, then the magnetizations \( M_x \) and
\( M_y \) measured with fields along \( x \) and \( y \) only depend on
\( p_1 \) and \( p_2 + p_3 = 1 - p_1 \). Of course, \( M_z \) measured with
field along \( z \) is independent of \( p_1 \). Fig. 3 indicates that
all three magnetizations increase monotonically up to at least 32 T.

Previous optical measurements \( [34] \) at the ordering
wavevector \( Q \) found two conventional spin-wave modes that
couple to the ground state through the magneti-
zation operator \( M = 2\mu_B \sum_i S_i \). These magnetic-
resonance (MR) modes are degenerate in zero field with a frequency of 1.07 THz and split almost linearly with increas-
ing field along \( y \), as shown in Fig. 4. For \( m = y \), the
MR modes are excited in two geometries: (i) with THz
fields \( E_0 || x \) and \( B_0 || z \) and (ii) with \( E_0 || z \) and \( B_0 || x \).
Those measurements also found an electromagnon (EM)
that couples to the ground state through the polarization
operator \( P \). The EM with zero-field frequency 1.41 THz
is only excited in geometry ii.

Because the exchange couplings already break every
degeneracy in the unit cell, the 16 predicted modes for a
single domain are non-degenerate. Therefore, the split
MR modes must come from different domains. This
was verified by measuring \( [35] \) the MR mode frequen-
cies as a function of the rotation angle \( \theta \) for field \( B =
B(\cos \theta, \sin \theta, 0) = B(x \cos \theta + y \sin \theta) \) in the labora-
tory reference frame. In practice, this is accomplished by ro-
tating the sample about \( c \) while keeping the field fixed.

FIG. 2: (Color online) A sideview view of the zero-field spin
configuration showing bitetrahedral \( c \)-axis chains \( \alpha \) and \( \beta \).

FIG. 3: (Color online) The measured (circles and squares) and
predicted (solid curves) magnetizations for field along \( [1, 0, 0] \),
\( [0, 1, 0] \), or \( [0, 0, 1] \).
TABLE I: Exchange and anisotropy parameters in meV.

| $\Delta$ | $J_1 = J_5$ | $J_2 = J_4$ | $J_3 = J_6$ | $J_7$ | $J_8$ | $J_{9}$ | $J_{10}$ | $J_{11} = J_{12}$ | $D^{\text{kg}}$ | $D^{\text{tri}}$ | $C^{\text{kg}}$ | $C^{\text{tri}}$ | $S_1^4$ | $A^{\text{tri}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| error | $0.185$ | $-91.5$ | $-10.8$ | $41.4$ | $-29.9$ | $187.8$ | $7.9$ | $108.0$ | $-6.7$ | $-0.67$ | $-1.24$ | $3.70$ | $0.77$ | $0.0004$ |

IV. FITTING RESULTS

Fits for the coupling parameters utilize the field dependence of $M$, the zero-field powder-diffraction data \cite{22}, the field dependence of the MR and EM modes at $\theta = \pi/2$ \cite{34}, and the MR mode frequencies at $\theta = 0$ and $\pi/3$ for 7, 12 and 15 T. The resulting exchange and anisotropy constants are provided in Table I and the corresponding zero-field spin state is plotted in Figs. 1(a-b). In contrast to the previously proposed \cite{22} spin state with zig-zag chains in the $ab$ plane containing spins 2, 3, 6, and 7, our spin state can be better described as an array of $c$-axis chains or connected bitetrahedra \cite{14,36} containing spins \{1, 2, 3, 4\} (chain $\alpha$) or \{5, 6, 7, 8\} (chain $\beta$) as sketched in Fig. 2. Chains are coupled by exchanges $J_9$, along $x$. As shown in Fig. 5 for 12 and 15 T, each hexagonal domain then contributes one MR branch with a period of $\pi$.

With field $\mathbf{B}_{\text{loc}} = B(\cos \psi, \sin \psi, 0) = B(a \cos \psi + b \sin \psi)$ in the domain reference frame, the upper MR mode in Fig. 4 corresponds to the $\psi = \pi/2$ mode for domain I while the lower MR mode corresponds to the degenerate $\psi = \pm \pi/6$ modes for domains II and III. Previously measured MR frequencies plotted in Fig. 4 at 12 T correspond to the diamond and triangular points in Fig. 5(b) at $\theta = \pi/2$. Cusps in the MR curves for each domain at $\psi = 0$ and $\pi$ are caused by flipping the $b$ component of the magnetization (see inset to Fig. 5(b)).
$J_{10}$, and $J_{12}$ in the $ab$ plane.

What explains the wide range of $J_i$ values? An orthorhombic distortion with $b/(a\sqrt{3}) - 1 \to 0.018$ as $T \to 0$ breaks the hexagonal symmetry of the $ab$ plane and explains the difference between the pairs $\{J_1, J_2\}$, $\{J_8, J_{11}\}$, and $\{J_{10}, J_{12}\}$. The difference between couplings like $\{J_7, J_8\}$ is caused by charge ordering: whereas $J_7$ couples moments 2 and 3 with $M_2 = M_3$, $J_8$ couples moments 2 and 4 with $M_2 \neq M_4$. Charge ordering also explains the difference between the pairs $\{J_2, J_3\}$ and $\{J_9, J_{10}\}$. Although not demanded by symmetry, we set $J_1 = J_5$, $J_2 = J_4$, $J_3 = J_6$, and $J_{11} = J_{12}$ because the spin state and excitations at $Q$ only depend on their averages.

Given other conditions, our fit chooses the spin state that matches the powder-diffraction data as closely as possible. At zero field, the predicted spin state has angles $\phi_1 = -0.83\pi$, $\phi_2 = 0.40\pi$, $\phi_3 = -0.23\pi$, and $\phi_4 = 0.62\pi$. Based exclusively on powder-diffraction data and symmetry constraints, the previously proposed spin state had $\phi_1 = -0.24\pi$, $\phi_2 = 0.37\pi$, and $\phi_4 = -0.44\pi$. In both cases, $\phi_{i+4} = \pi - \phi_i$ ($i = 1, \ldots, 4$) so that the moment $M_i$ lies along the $b$ axis. As shown in Table II, our spin state does not satisfy the powder diffraction data quite as well as the earlier state, primarily because it underestimates the powder diffraction peak $I(112)$.

For the previous spin state, $\chi^2$ is minimized by Lorentzian form factors with $Q_1/4\pi = 0.088$ Å$^{-1}$, $Q_2/4\pi = Q_3/4\pi = 0.095$ Å$^{-1}$, and $Q_4/4\pi = 0.088$ Å$^{-1}$ for spins $S_n$. For the new spin state, $Q_1/4\pi = 0.052$ Å$^{-1}$, $Q_2/4\pi = Q_3/4\pi = 0.224$ Å$^{-1}$, and $Q_4/4\pi = 0.102$ Å$^{-1}$. All are smaller than the scale $Q_0/4\pi \approx 0.3$ Å$^{-1}$ measured by Khan and Erickson for Co$^{2+}$ in CoO.

Our results indicate that the exchange coupling $J_8$ $\approx 188$ meV between moments 2 (Co$^{2+}$, $S_2 = 1$) and 4 (Co$^{3+}$/Co$^{2+}$, $S_4 = 1.2$) is strongly ferromagnetic and larger in magnitude even than the 155 meV antiferromagnetic coupling found in the cuprate Nd$_2$CuO$_4$ [39]. The strength of this coupling might be explained by the double-exchange mediated hopping of ligand holes $L$ from site 4 to 2. Bear in mind, however, that the estimated exchange parameters would be significantly reduced if the fits were performed with $S = 3/2$ for all Co spins. In particular, $J_8$ would then fall from 188 to 100 meV.

Except for $J_{10}$, the five largest exchange couplings $J_1 = J_5 \approx -92$ meV, $J_3 = J_6 \approx 41$ meV, and $J_8 \approx 188$ meV lie within connected bitetrahedral, $c$-axis chains. Inside each chain, competing interactions between spins 1, 2, and 4 produce a non-collinear spin state.

Although occupying a triangular lattice, chains $a$ and $b$ are magnetically ordered with moments $M^{\text{th}} = (\pm 1.18, 1.33, 0)_{\text{BH/f.u.}}$. These chains are primarily coupled by the strongly ferromagnetic interaction $J_{10} \approx 108$ meV between nearly parallel spins $\{4, 6\}$ ($\phi_4 = 0.62\pi$, $\phi_6 = 0.60\pi$) and $\{2, 8\}$ ($\phi_2 = 0.40\pi, \phi_8 = 0.38\pi$). Above $T_c = 70$ K, the short-range order within each chain may be responsible for the large, negative Curie-Weiss temperature $\Theta_{\text{CW}} \approx -1720$ or $-890$ K, the larger than expected Curie constant [26], and the susceptibility anomaly at 360 K suggestive of short-range magnetic order far above $T_c$.

Comparison between the theoretical and experimental results for the magnetization in Fig. 3 suggests that roughly 20% of the sample is in domain I. Different domain populations or even orthorhombic twinning in other samples may explain the discrepancies between the reported magnetization measurements [22,31,63].

Easy-axis anisotropies A and C favor ferrimagnetic alignment along $b$ rather than $a$. The spin-flop (SF) field required to flip the spins towards the $a$ direction must increase as the field along $b$ increases [40]. As shown in the inset to Fig. 5(a), $B_{\text{SF}}(\psi)$ then increases with $\psi$. If $B_{\text{SF}}(\psi = 0) < 15$ T, then the MR spectrum for 15 T would show a discontinuity at the transition from a low-field (LF) to a high-field (HF) state below some critical value of $\psi$. Since the MR mode frequencies in Fig. 5(a) do not exhibit any discontinuities as a function of $\psi$, we conclude that $B_{\text{SF}}(\psi = 0)$ exceeds 15 T and probably, based on the smooth dependence of the magnetizations on field, exceeds 32 T as well. The apparent small size of $B_{\text{SF}}$ [24,11] must reflect the net magnetization of all three domains.

Predicted modes below 5 THz are plotted in Fig. 4. The Goldstone modes for all three domains are lifted by in-plane anisotropies to become the MR modes with zero-field frequencies of 1.07 THz. As remarked earlier, the lower MR mode comes from domains II and III while the upper MR mode comes from domain I. Below 3.5 THz, one EM mode is produced in domain I and another in domains II and III. The degenerate EM modes from domains II and III dominate the optical absorption. The predicted field dependence of the upper MR mode is quite close to the observed dependence. But the predicted curvatures of the lower MR mode and the EM mode, both from domains II and III, is not observed.

V. SPIN-INDUCED ELECTRIC POLARIZATION

Below the ferrimagnetic transition, CaBaCo$_4$O$_7$ is reported to develop a very large spin-induced polarization $\sim 1700$ nC/cm$^2$, which is surpassed in type I multiferroics only by the conjectured spin-induced polarization $\sim 3000$ nC/cm$^2$ of BiFeO$_3$. Other measurements indicate that the spin-induced polarization of CaBaCo$_4$O$_7$ ranges from 320 nC/cm$^2$ [32] to 900 nC/cm$^2$ [12].

The electric-field dependence of any interaction term in the spin Hamiltonian $\mathcal{H}$ can induce an electric polarization below $T_c$. However, the electric-field dependence of the easy-plane anisotropy $D$ cannot explain the spin-induced polarization along $c$ because the expectation value of $P_i = \kappa S_i c^2$ with $\kappa = -\partial D/\partial E_c$ would vanish in zero magnetic field when all the spins lie in the...
TABLE II: Ratios of powder-diffraction peak intensities

<table>
<thead>
<tr>
<th></th>
<th>I(002)/I(101)</th>
<th>I(012)/I(101)</th>
<th>I(111)/I(101)</th>
<th>I(112)/I(101)</th>
<th>I(121)/I(101)</th>
<th>I(122)/I(101)</th>
<th>Mn(μmO/f.u.)</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>experimental</td>
<td>0.344</td>
<td>0.326</td>
<td>0.322</td>
<td>0.477</td>
<td>0.262</td>
<td>0.404</td>
<td></td>
<td></td>
</tr>
<tr>
<td>previous</td>
<td>0.286</td>
<td>0.414</td>
<td>0.384</td>
<td>0.411</td>
<td>0.232</td>
<td>0.427</td>
<td>0.88</td>
<td>0.021</td>
</tr>
<tr>
<td>current</td>
<td>0.360</td>
<td>0.380</td>
<td>0.378</td>
<td>0.286</td>
<td>0.313</td>
<td>0.449</td>
<td>1.33</td>
<td>0.047</td>
</tr>
</tbody>
</table>

ab plane. Easy-axis anisotropy A or C in the ab plane could produce a spin-induced electric polarization perpendicular to c. But the EM mode would then become observable for a THz electric field in the ab plane, contrary to measurements.

As conjectured previously, the spin-induced polarization in CaBaCoO₇ must then be generated by the dependence of the exchange interactions J_ij on an electric field, called magnetostriction. Coupling constant \( \lambda_{ij} = \partial J_{ij}/\partial E_c \) for bond \{i, j\} is associated with a spin-induced polarization \( \vec{\lambda}_{ij} \) per site of \( P^{ij}_0 = \lambda_{ij} \vec{S}_i \cdot \vec{S}_j /4 \), which accounts for the four equivalent bonds per unit cell. Expanding in the electric field \( E_c \) yields an interaction term \(-E_c \lambda_{ij} \vec{S}_i \cdot \vec{S}_j \), linear in the electric field and quadratic in the spin operators.

Taking \( \langle 0 \rangle \) as the ground state and \( |n \rangle \) as the excited spin-wave state, the MR matrix element \( \langle n|M_a|0 \rangle \) mixes with the EM matrix element \( \langle n|P_\omega^\alpha|0 \rangle \) for domains II and III but not for domain I. Therefore, our model can explain the strong asymmetry \( \approx \text{Re} \{ \langle n|M\cdot B_\omega|0 \rangle |0|P_\omega^\alpha|n \rangle \} \) in the absorption of counter-propagating light waves \( \approx \text{Im} \{ \langle n|M\cdot B_\omega|0 \rangle |0|P_\omega^\alpha|n \rangle \} \) for the lower observed MR mode in geometry \( \omega \) with \( B_\omega \perp c \). But it cannot explain the observed asymmetry of this mode in geometry \( \omega \) with \( B_\omega \perp c \).

How can we estimate the coupling constants \( \lambda_{ij} \) and the spin-induced electric polarization? The optical absorption of any mode in domain \( \ell \) is proportional to \( P_\ell^2 \) because each matrix element is separately proportional to \( P_\ell \). At nonzero field, the EM mode absorption is proportional to \( P_\ell^2 + p_3^2 + p_5^2 \) while the upper MR mode absorption is proportional to \( P_\ell^2 \). At zero field, all domains have the same mode spectrum so that both the MR and EM mode absorptions are proportional to \( P_\ell^2 + p_3^2 + p_5^2 \). Experimentally, the ratio \( r \) of the absorption of the EM mode to the absorption of the upper MR mode rises from \( r = 7.5 \) at 0 T to \( r = 35 \) at 10 T. This growth is explained by the \( B > 0 \) ratio \( (P_\ell^2 + p_3^2)/P_\ell^2 \approx 10 \pm 5 \) for \( p_1 = 0.185 \pm 0.071 \) and \( p_2 = p_3 = (1 - p_1)/2 \).

At both 0 and 10 T, the only sets of bonds that generate spin-induced polarizations of the right magnitude are \{2, 7\} and \{3, 4\}. Each of those bonds couples adjacent c-axis chains through pairs of spins that are almost anti-parallel. From the relative absorptions \( r \) at 0 or 10 T, we estimate that \( \langle P_\ell^2 \rangle \approx 2350 \) or 1960 nC/cm² and \( \langle P_\omega^3 \rangle \approx 2110 \) or 1730 nC/cm². Results for both sets of bonds are consistent with the recently observed polarization of 1700 nC/cm². By contrast, density-functional theory predicts that the spin-induced polarization along c is 460 nC/cm². The spin-induced polarization should remain fairly constant with applied magnetic field, decreasing by about 1% for a 10 T field along b.

VI. CONCLUSION

We have presented a nearly complete solution for the magnetization, spin state, and mode frequencies of the swedenborgite CaBaCoO₇. An orthorhombic distortion above \( T_c \) partially relieves the geometric frustration on the kagome and triangular layers and allows ferromagnetism and ferroelectricity to coexist below \( T_c \). Although occupying a triangular lattice, bitetrahedral c-axis chains are ferrimagnetically ordered in the ab plane. Competing interactions within each chain produce non-collinear spin states. Sets of bonds coupling those chains are responsible for the large spin-induced polarization of CaBaCoO₇.

Despite its fixed permanent electric polarization, this swedenborgite may yet have important technological applications utilizing the large changes \( \approx \text{Im} \{ \langle n|M\cdot B_\omega|0 \rangle |0|P_\omega^\alpha|n \rangle \} \) in the spin-induced polarization when a modest magnetic field < 1 T is applied along b just below \( T_c \). A big jump in the polarization should also be produced just below \( T_c \) by rotating a fixed magnetic field about the c axis. Above all, our work illuminates a pathway to develop other functional materials with sizeable magnetic moments and electrical polarizations.

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While the coplanar LF spin state has a lower energy than the HF state below 32 T, it becomes locally unstable to a buckled state with spins canted out of the plane. Based on the symmetry of adjacent layers, it is easy to show that the polarization operator $P_{ij}$ associated with bond $\{i,j\}$ has components $P_{a}^{12} \propto C_{12} - C_{56} - C_{1'2'} + C_{5'6'}$, $P_{b}^{12} \propto C_{12} + C_{56} - C_{1'2'} - C_{5'6'}$, and $P_{c}^{12} \propto C_{12} + C_{56} + C_{1'2'} + C_{5'6'}$, where $C_{ij} = \mathbf{S}_{i} \cdot \mathbf{S}_{j}$. Similar relations hold for other bonds. Only the $c$ component $P_{c}^{ij}$ can produce a static polarization but all three components may contribute to the off-diagonal polarization matrix elements $\langle 0 | P_{ij}^{l} | n \rangle$ ($n \neq 0$).